

TITLE OF THE INVENTION

ACENAPHTHYLENE DERIVATIVE, POLYMER, AND
ANTIREFLECTION FILM-FORMING COMPOSITION

5

BACKGROUND OF THE INVENTION

Field of the Invention

The present invention relates to
acetoxymethylacenaphthylene, hydroxymethylacenaphthylene, a
polymer prepared from the acetoxymethylacenaphthylene or
10 hydroxymethylacenaphthylene, and an antireflection
film-forming composition comprising the polymer suitable for
use in microfabrication using a lithography process which
utilizes various radiations, particularly for manufacturing
highly integrated circuit elements.

15

Description of Background Art

Production of polyacenaphthylene by polymerizing
acenaphthylene and production of copolymers by copolymerizing
acenaphthylene with styrene, maleic anhydride, or the like are
well known in the art.

20

Such acenaphthylene polymers and copolymers
(hereinafter collectively referred to as (co)polymers) are
highly reactive due to their unique structure. Chemical
reactions of such (co)polymers with various reactive reagents
have been investigated and details of their properties such as
25 luminous actions have been reported. Various materials
possessing properties such as low hygroscopicity, low
birefringence, and low dielectric constant, as well as

utilization of such materials have been developed.

Providing acenaphthylene derivatives possessing various functional groups useful as raw materials for manufacturing acenaphthylene (co)polymers is very important from academic and industrial viewpoints in developing the acenaphthylene (co)polymers that are highly reactive and expected to have various characteristics. Various acenaphthylene derivatives having an aromatic ring substituted with a hydroxyl group, alkyl group, halomethyl group, halogen, or the like have already been synthesized.

However, no acenaphthylene derivatives having an aromatic ring substituted with an acetoxymethyl group or hydroxymethyl group have been reported heretofore.

The fabrication size in a lithography process for manufacturing integrated circuit elements is becoming smaller to achieve a higher degree of integration. In the lithography process, a resist composition solution is applied to a substrate, a mask pattern is transcribed on the resist by a stepper (reducing projection aligner), and the resist is developed using a suitable developer to obtain a desired pattern. However, the substrate having a high reflectance such as aluminum, aluminum-silicon alloy, aluminum-silicon-copper alloy, polysilicon, or tungsten silicide used in this process reflects radiation on the surface and produces halation on a resist pattern, making it impossible to precisely reproduce a fine resist pattern.

To overcome this problem, a method of providing an

antireflection film that can absorb radiation reflected on the surface of the substrate under the resist film to be formed on the substrate has been proposed. Inorganic films such as a titanium film, titania film, titanium nitride film, chromium
5 oxide film, carbon film, and α -silicon film formed by vacuum deposition, CVD, sputtering, or the like are known as such an antireflection film. These inorganic antireflection films, however, have drawbacks such as conductivity which precludes these films from being used for production of integrated
10 circuits and requirement of a special apparatus for forming such as a vacuum deposition apparatus, CVD apparatus, and sputtering apparatus.

As a material overcoming these drawbacks of inorganic antireflection films, an organic antireflection film made from
15 a polyamide acid (co)polymer or polysulfone (co)polymer and a dye has been proposed (see Japanese Patent Application Laid-open No. 59-93448, for example). This organic antireflection film has no conductivity. In addition, since the composition from which the film is formed is dissolvable
20 in common solvents, the composition can be applied to a substrate as easily as a resist composition solution without requiring a special apparatus.

However, since the organic antireflection film made from a polyamide acid (co)polymer or polysulfone (co)polymer and a
25 dye limits the amount of the dye that can be added, the film cannot sufficiently prevent halation and standing waves. In addition, because such an organic film migrates with a resist

film in a slight amount (a phenomenon known as intermixing), a resist pattern may have an impaired sectional configuration (an impaired pattern profile) such as inadequate dyeing and a skirt shape.

5 On the other hand, a polymer having an acenaphthylene skeleton is known to overcome the above-described problems to a considerable extent, if applied to an antireflection film (see Japanese Patent Applications Laid-open No. 2000-143937 and No. 2001-402933, for example). The antireflection film, however,
10 cannot necessarily overcome the problem of intermixing.

As a means for overcoming this problem, a method of crosslinking the polymer having an acenaphthylene skeleton with formaldehyde or the like is thought to be effective. This method, however, may impair storage stability of the
15 antireflection film-forming composition stored in the form of a solution.

Development of an improved antireflection film that can overcome the problems in conventional technologies and development of a polymer useful as a polymer component for such
20 an antireflection film have therefore been desired.

The subject of the present invention is to overcome the above-described problems in conventional technologies and provide an antireflection film-forming composition exhibiting high antireflection effect and capable of forming resist
25 patterns excelling in resolution, pattern configuration, and the like, without intermixing, to provide a polymer useful particularly as a component for the antireflection film-forming

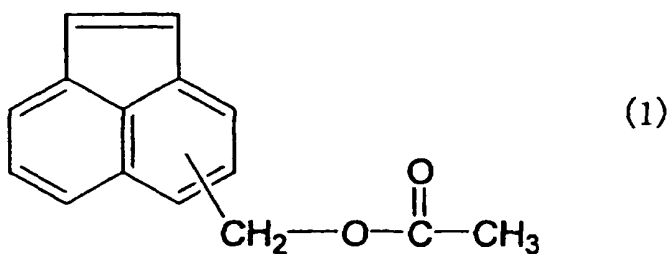
composition, and to provide acenaphthylene derivatives useful particularly as a raw material or an intermediate for the polymer.

As a result of extensive studies to solve the above
5 problems, the inventors of the present invention have found that a novel acenaphthylene derivative easily synthesized from a readily available acenaphthene by a process involving well-known organic synthesis reactions is very useful as a raw material or an intermediate for a polymer that can effectively
10 solve the above problems relating to antireflection films. The inventors have further found that a novel polymer having an aromatic ring with a specific substituent that can be produced from the acenaphthylene derivative exhibits a high absorbance of an excimer laser or other radiations and a high refractive
15 index in comparison with conventional antireflection films, and that excellent antireflection films can be produced by using the polymer as an antireflection film-forming composition. The findings have led to the completion of the present invention.

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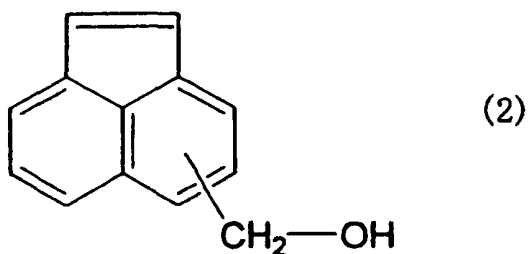
SUMMARY OF THE INVENTION

An object of the present invention is to provide acetoxymethylacenaphthylene of the following formula (1).



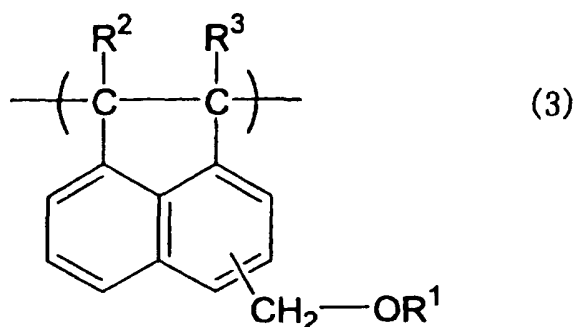
Another object of the present invention is to provide hydroxymethylacenaphthylene of the following formula (2).

5



A still another object of the present invention is to provide a polymer (hereinafter referred to as "polymer (I)") having a structural unit of the following formula (3) (hereinafter referred to as "structural unit (3)") and having a polystyrene-reduced weight average molecular weight determined by gel permeation chromatography (GPC) in the range of 500-10,000,

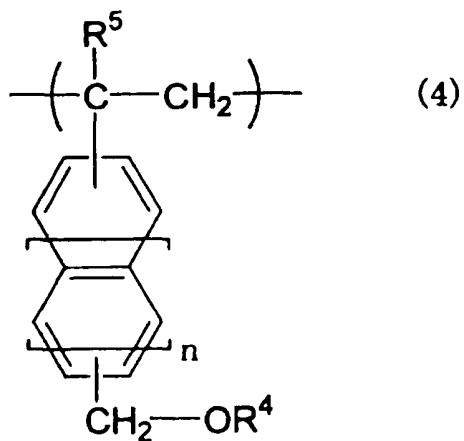
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wherein R¹ represents a hydrogen atom or a monovalent organic group and R² and R³ individually represent a monovalent atom
 5 or a monovalent organic group.

Yet another object of the present invention is to provide an antireflection film-forming composition comprising the polymer (I) and a solvent.

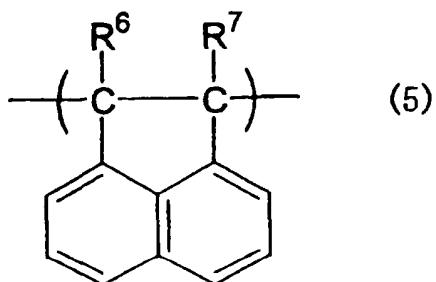
A further object of the present invention is to provide
 10 an antireflection film-forming composition comprising a polymer (hereinafter referred to as "polymer (II)") having a structural unit of the following formula (4) (hereinafter referred to as "structural unit (4)") and a solvent,



15

wherein R^4 is a hydrogen atom or a monovalent organic group,
 R^5 is a monovalent atom or a monovalent organic group, and n
is 0 or 1.

5 A still further object of the present invention is to
provide an antireflection film-forming composition comprising
at least one polymer selected from the group consisting of a
polymer (hereinafter referred to as "polymer (III)") having the
structural unit (3) and the structural unit (4), a polymer
10 (hereinafter referred to as "polymer (IV)") having the
structural unit (3) and a structural unit of the following
formula (5) (hereinafter referred to as "structural unit (5)"),
and a polymer (hereinafter referred to as "polymer (V)") having
the structural unit (4) and the structural unit (5) and a
15 solvent,



wherein R^6 and R^7 individually represent a monovalent atom or
20 a monovalent organic group.

DETAILED DESCRIPTION OF THE INVENTION AND
PREFERRED EMBODIMENTS

The present invention is described below in detail.

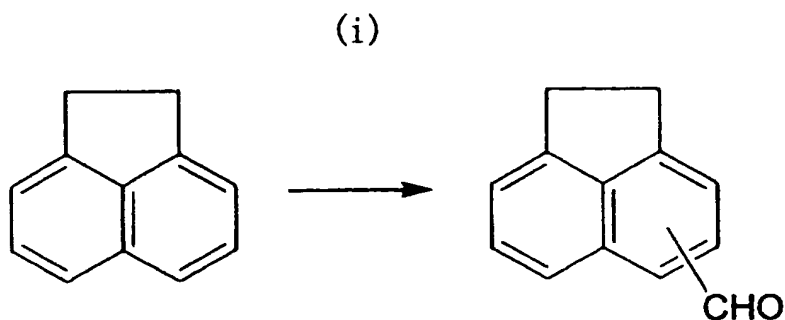
Acetoxymethylacenaphthylene and hydroxymethylacenaphthylene

The acetoxymethyl group in the formula (1) or
5 hydroxymethyl group in the formula (2) bonds to either one of
the 3 to 5 positions of the acenaphthylene.

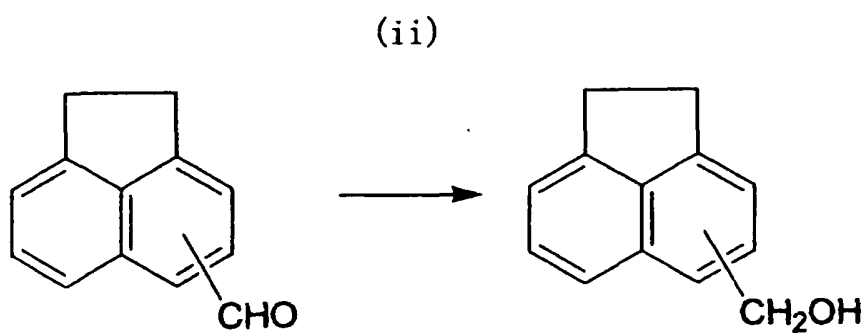
The acetoxymethylacenaphthylene of the formula (1)
(hereinafter referred to as "acetoxymethylacenaphthylene
(1)") can be synthesized by a process comprising the following
10 steps 1-4. The hydroxymethylacenaphthylene of the formula (2)
(hereinafter referred to as "hydroxymethylacenaphthylene
(2)") can be synthesized by the following step 5.

Step 1: Acenaphthene is formylated by a conventional
method as shown in the following formula (i).

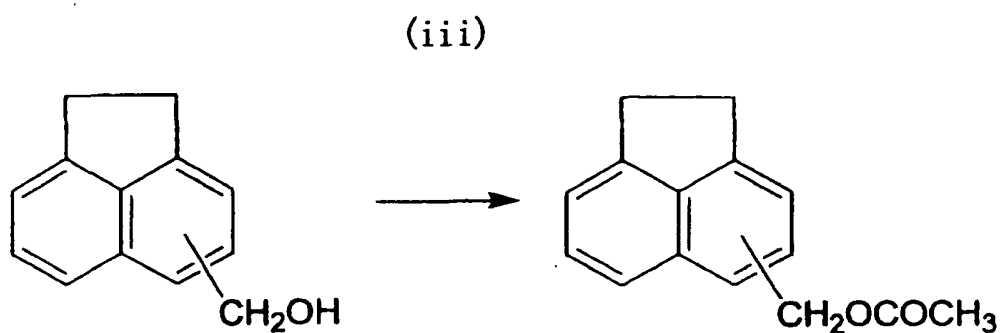
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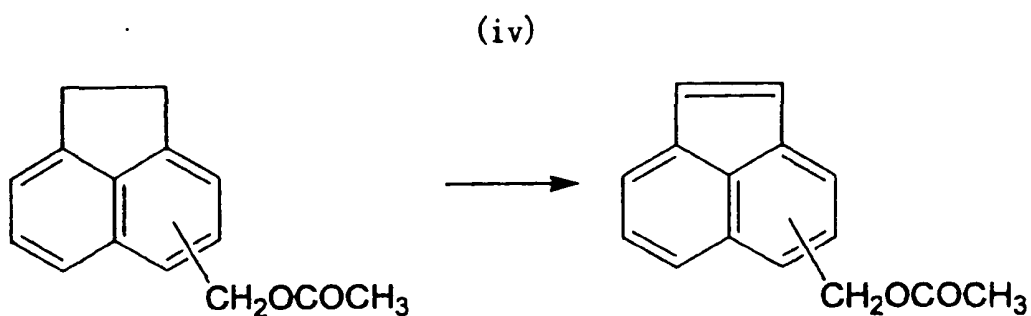
Step 2: The formyl group in the formyl acenaphthene
obtained in Step 1 is reduced by a conventional method to obtain
20 hydroxymethylacenaphthene as shown in the following formula
(ii).



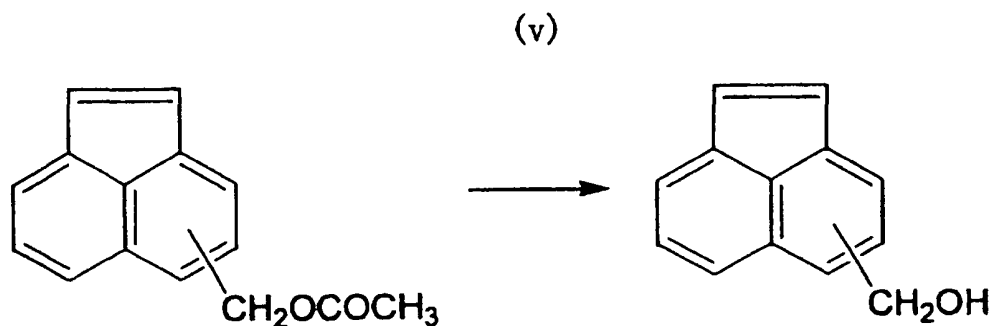
Step 3: The hydroxyl group in the hydroxymethylacenaphthene obtained in Step 2 is acetylated by a conventional method to obtain acetoxymethylacenaphthene as shown in the following formula (iii).



Step 4: The acetoxymethylacenaphthene obtained in Step 3 is dehydrogenated by a conventional method to obtain acetoxymethylacenaphthylene (1) as shown in the following formula (iv).



Step 5: The acetoxy group in the
 acetoxymethylenaphthylene obtained in Step 4 is hydrolyzed
 5 by a conventional method to obtain hydroxymethylenaphthylene
 (2) as shown in the following formula (v).



10 Acetoxymethylenaphthylene (1) can be suitably used not
 only as a raw material or an intermediate material for
 manufacturing the polymer (I), polymer (III), and polymer (IV),
 but also as a raw material for synthesizing
 hydroxymethylenaphthylene (2).

15 Acetoxymethylenaphthylene (1) is also used as a raw material
 or an intermediate for synthesizing other related
 acenaphthylene derivatives.

Hydroxymethylenaphthylene (2) can be suitably used not

only as a raw material or an intermediate material for manufacturing the polymer (I), polymer (III), and polymer (IV), but also as a raw material for synthesizing acetoxymethylacenaphthylene (1).

- 5 Hydroxymethylacenaphthylene (2) is also used as a raw material or an intermediate for synthesizing other related acenaphthylene derivatives.

Polymer (I)

- 10 As the monovalent organic group represented by R^1 in the structural unit (3), groups having 1-10 carbon atoms are preferable. Examples of the preferable organic group are a phenyl group, alkyl group, alkenyl group, acyl group, and groups in which one or more hydrogen atoms on the phenyl group, alkyl
15 group, or alkenyl group are replaced by one or more, the same or different, substituents such as a halogen atom, hydroxyl group, mercapto group, carboxyl group, nitro group, and sulfonic acid group.

- As the alkyl group, linear or branched alkyl groups having
20 1-6 carbon atoms are preferable. A methyl group, ethyl group, n-propyl group, i-propyl group, n-butyl group, i-butyl group, sec-butyl group, and t-butyl group, for example, are particularly preferable.

- As the alkenyl group, linear or branched alkenyl groups
25 having 2-6 carbon atoms are preferable. Particularly preferable examples are a vinyl group, allyl group, methallyl group, 1-butenyl group, and 2-butenyl group.

As the acyl group, aliphatic or aromatic acyl groups having 2-6 carbon atoms are preferable. Particularly preferable examples are an acetyl group, propionyl group, butyryl group, and benzoyl group.

5 As examples of the monovalent atom represented by R^2 or R^3 in the structural unit (3), a hydrogen atom and a halogen atom such as a fluorine atom, chlorine atom, or bromine atom can be given.

As examples of the monovalent organic group represented
10 by R^2 or R^3 , the same groups as those previously given for the monovalent organic group represented by R^1 can be given.

Particularly preferable groups for R^1 in the structural unit (3) are a hydrogen atom, methyl group, acetyl group, and the like.

15 Preferable groups for R^2 or R^3 are a hydrogen atom, methyl group, phenyl group, and the like.

The polymer (I) can be prepared by polymerizing an acenaphthylene corresponding to the structural unit (3), optionally together with a copolymerizable unsaturated monomer
20 by radical polymerization, anionic polymerization, cationic polymerization, or the like using an appropriate process such as a mass polymerization process or solution polymerization process.

The polymer (I) having the structural unit (3) in which
25 the R^1 group is a hydrogen atom can be produced by hydrolyzing the acetoxy group of the polymer (I) having the structural unit (3) in which the R^1 group is an acetyl group by a conventional

method. The polymer (I) having the structural unit (3) in which the R¹ group is an acetyl group can be produced by acetylating the hydroxyl group of the polymer (I) having the structural unit (3) in which the R¹ group is a hydrogen atom by a conventional
5 method.

The following compounds can be given as examples of the acenaphthylene corresponding to the structural unit (3):
hydroxymethylacenaphthylenes such as
3-hydroxymethylacenaphthylene,
10 4-hydroxymethylacenaphthylene,
5-hydroxymethylacenaphthylene,
1-methyl-3-hydroxymethylacenaphthylene,
1-methyl-4-hydroxymethylacenaphthylene,
1-methyl-5-hydroxymethylacenaphthylene,
15 1-methyl-6-hydroxymethylacenaphthylene,
1-methyl-7-hydroxymethylacenaphthylene,
1-methyl-8-hydroxymethylacenaphthylene,
1,2-dimethyl-3-hydroxymethylacenaphthylene,
1,2-dimethyl-4-hydroxymethylacenaphthylene,
20 1,2-dimethyl-5-hydroxymethylacenaphthylene,
1-phenyl-3-hydroxymethylacenaphthylene,
1-phenyl-4-hydroxymethylacenaphthylene,
1-phenyl-5-hydroxymethylacenaphthylene,
1-phenyl-6-hydroxymethylacenaphthylene,
25 1-phenyl-7-hydroxymethylacenaphthylene,
1-phenyl-8-hydroxymethylacenaphthylene,
1,2-diphenyl-3-hydroxymethylacenaphthylene,

1,2-diphenyl-4-hydroxymethylacenaphthylene, and
1,2-diphenyl-5-hydroxymethylacenaphthylene;
acetoxymethylacenaphthylenes such as
3-acetoxymethylacenaphthylene,
5 4-acetoxymethylacenaphthylene,
5-acetoxymethylacenaphthylene,
1-methyl-3-acetoxymethylacenaphthylene,
1-methyl-4-acetoxymethylacenaphthylene,
1-methyl-5-acetoxymethylacenaphthylene,
10 1-methyl-6-acetoxymethylacenaphthylene,
1-methyl-7-acetoxymethylacenaphthylene,
1-methyl-8-acetoxymethylacenaphthylene,
1,2-dimethyl-3-acetoxymethylacenaphthylene,
1,2-dimethyl-4-acetoxymethylacenaphthylene,
15 1,2-dimethyl-5-acetoxymethylacenaphthylene,
1-phenyl-3-acetoxymethylacenaphthylene,
1-phenyl-4-acetoxymethylacenaphthylene,
1-phenyl-5-acetoxymethylacenaphthylene,
1-phenyl-6-acetoxymethylacenaphthylene,
20 1-phenyl-7-acetoxymethylacenaphthylene,
1-phenyl-8-acetoxymethylacenaphthylene,
1,2-diphenyl-3-acetoxymethylacenaphthylene,
1,2-diphenyl-4-acetoxymethylacenaphthylene, and
1,2-diphenyl-5-acetoxymethylacenaphthylene;
25 methoxymethylacenaphthylenes such as
3-methoxymethylacenaphthylene,
4-methoxymethylacenaphthylene,

5-methoxymethylacenaphthylene,
 1-methyl-3-methoxymethylacenaphthylene,
 1-methyl-4-methoxymethylacenaphthylene,
 1-methyl-5-methoxymethylacenaphthylene,
 5 1-methyl-6-methoxymethylacenaphthylene,
 1-methyl-7-methoxymethylacenaphthylene,
 1-methyl-8-methoxymethylacenaphthylene,
 1,2-dimethyl-3-methoxymethylacenaphthylene,
 1,2-dimethyl-4-methoxymethylacenaphthylene,
 10 1,2-dimethyl-5-methoxymethylacenaphthylene,
 1-phenyl-3-methoxymethylacenaphthylene,
 1-phenyl-4-methoxymethylacenaphthylene,
 1-phenyl-5-methoxymethylacenaphthylene,
 1-phenyl-6-methoxymethylacenaphthylene,
 15 1-phenyl-7-methoxymethylacenaphthylene,
 1-phenyl-8-methoxymethylacenaphthylene,
 1,2-diphenyl-3-methoxymethylacenaphthylene,
 1,2-diphenyl-4-methoxymethylacenaphthylene, and
 1,2-diphenyl-5-methoxymethylacenaphthylene;
 20 3-phenoxyethylacenaphthylene,
 4-phenoxyethylacenaphthylene,
 5-phenoxyethylacenaphthylene,
 3-vinyloxyethylacenaphthylene,
 4-vinyloxyethylacenaphthylene, and
 25 5-vinyloxyethylacenaphthylene.

Of these acenaphthylenes,
 3-hydroxyethylacenaphthylene,

4-hydroxymethylacenaphthylene,
5-hydroxymethylacenaphthylene,
3-acetoxymethylacenaphthylene,
4-acetoxymethylacenaphthylene,
5 5-acetoxymethylacenaphthylene,
3-methoxymethylacenaphthylene,
4-methoxymethylacenaphthylene, and
5-methoxymethylacenaphthylene are particularly preferable.

These acenaphthylenes may be used either individually
10 or in combinations of two or more.

As other copolymerizable unsaturated compounds used for
the polymer (I), aromatic vinyl compounds corresponding to the
later described structural unit (4) and acenaphthenes
corresponding to the later described structural unit (5) are
15 preferable.

The following compounds can be given as examples of the
other copolymerizable unsaturated compounds:
aromatic vinyl compounds such as styrene, α -methylstyrene,
2-methylstyrene, 3-methylstyrene, 4-methylstyrene,
20 1-vinylnaphthalene, 2-vinylnaphthalene, 9-vinylanthracene,
and 9-vinylcarbazole; vinyl esters such as vinyl acetate, vinyl
propionate, and vinyl caprate; cyanated vinyl compounds such
as (meth)acrylonitrile, α -chloroacrylonitrile, and cyanated
vinylidene; unsaturated carboxylic acid esters such as methyl
25 (meth)acrylate, ethyl (meth)acrylate, n-propyl (meth)acrylate,
isopropyl (meth)acrylate, n-butyl (meth)acrylate, t-butyl
(meth)acrylate, n-hexyl (meth)acrylate, and glycidyl

(meth)acrylate; unsaturated group-containing unsaturated carboxylates such as ethylene glycol di(meth)acrylate, propylene glycol di(meth)acrylate, vinyl (meth)acrylate, and dimethyl·vinyl·(meth)acryloyloxymethylsilane;

5 halogen-containing vinyl compounds such as 2-chloroethyl vinyl ether, vinyl chloroacetate, and allyl chloroacetate;

hydroxyl group-containing vinyl compounds such as 2-hydroxyethyl (meth)acrylate, 2-hydroxypropyl (meth)acrylate, and (meth)allyl alcohol; amide

10 group-containing vinyl compounds such as (meth)acryl amide and crotonic acid amide; and carboxyl group-containing vinyl compounds such as mono-[2-(meth)acryloyloxyethyl] succinate, mono-[2-(meth)acryloyloxyethyl] maleate, and mono-[2-(meth)acryloyloxyethyl] phthalate.

15 These other copolymerizable unsaturated compounds may be used either individually or in combination of two or more.

The amount of the structural unit derived from such other copolymerizable unsaturated compounds in the polymer (I) is preferably 80 mol% or less, more preferably 60 mol% or less,
20 and particularly preferably 40 mol% or less of the total amount of the structural units.

The polystyrene-reduced weight average molecular weight of the polymer (I) measured by gel permeation chromatography (hereinafter abbreviated as "Mw") is preferably 500-10,000, and
25 preferably 1,000-5,000.

The molecular chains of the polymer (I) are crosslinkable by heating or exposure to light and, therefore, the polymer (I)

is useful particularly for the antireflection film-forming composition described later. In addition, the polymer (I) can be used in paints, adhesives, insulating materials, formed articles, and the like either individually or in combination
5 with other curable resins and curable rubbers.

Antireflection film-forming composition

The antireflection film-forming composition of the present invention comprises (a) the polymer (I) and a solvent,
10 (b) polymer (II) and a solvent, or (c) at least one polymer selected from the group consisting of the polymer (III), polymer (IV), and the polymer (V) and a solvent.

The polymers (II) to (V) and the solvent that make up the antireflection film-forming composition of the present
15 invention will now be described.

Polymer (II)

As examples of the monovalent organic group represented by R^4 in the structural unit (4), the same groups as those previously given for the group R^1 in the structural unit (3)
20 can be given. As examples of the monovalent atom or monovalent organic group represented by R^5 , the same monovalent atoms or monovalent groups as those previously given for the group R^2 and R^3 in the structural unit (3) can be given.

A hydrogen atom, methyl group, and the like are
25 particularly preferable for R^4 in the structural unit (4).

A hydrogen atom, methyl group, and the like are preferable as R^5 group.

The polymer (II) can be prepared by polymerizing an aromatic vinyl compound corresponding to the structural unit (4), optionally together with a copolymerizable unsaturated monomer by radical polymerization, anionic polymerization, 5 cationic polymerization, or the like using an appropriate process such as a mass polymerization process or solution polymerization process.

The polymer (II) having the structural unit (4) in which the R⁴ group is a hydrogen atom can be produced by hydrolyzing 10 the acetoxy group of the polymer (II) having the structural unit (4) in which the R⁴ group is an acetyl group by a conventional method. The polymer (II) having the structural unit (4) in which the R⁴ group is an acetyl group can be produced by acetylating the hydroxyl group of the polymer (II) having the 15 structural unit (4) in which the R⁴ group is a hydrogen atom by a conventional method.

Preferable examples of the aromatic vinyl compound corresponding to the structural unit (4) include: hydroxymethylstyrene compounds such as 2-hydroxymethylstyrene, 20 3-hydroxymethylstyrene, 4-hydroxymethylstyrene, 2-hydroxymethyl- α -methylstyrene, 3-hydroxymethyl- α -methylstyrene, and 4-hydroxymethyl- α -methylstyrene; methoxymethylstyrene compounds such as 2-methoxymethylstyrene, 25 3-methoxymethylstyrene, 4-methoxymethylstyrene, 2-methoxymethyl- α -methylstyrene, 3-methoxymethyl- α -methylstyrene, and

4-methoxymethyl- α -methylstyrene; styrene compounds such as
 4-phenoxyethylstyrene, 4-phenoxyethyl- α -methylstyrene,
 4-vinyloxyethylstyrene, 4-vinyloxyethyl- α -methylstyrene,
 4-acetoxyethylstyrene, and 4-acetoxyethyl- α -methylstyrene;

5 hydroxymethyl vinyl naphthalene compounds such as
 4-hydroxymethyl-1-vinylnaphthalene,
 7-hydroxymethyl-1-vinylnaphthalene,
 8-hydroxymethyl-1-vinylnaphthalene,
 1-hydroxymethyl-2-vinylnaphthalene,
 10 1-hydroxymethyl-3-vinylnaphthalene,
 1-hydroxymethyl-4-vinylnaphthalene,
 1-hydroxymethyl-5-vinylnaphthalene,
 1-hydroxymethyl-6-vinylnaphthalene,
 1-hydroxymethyl-7-vinylnaphthalene,
 15 1-hydroxymethyl-8-vinylnaphthalene,
 2-hydroxymethyl-3-vinylnaphthalene,
 2-hydroxymethyl-4-vinylnaphthalene,
 2-hydroxymethyl-5-vinylnaphthalene,
 2-hydroxymethyl-6-vinylnaphthalene,
 20 2-hydroxymethyl-7-vinylnaphthalene,
 4-hydroxymethyl-1-isopropenylnaphthalene,
 7-hydroxymethyl-1-isopropenylnaphthalene, and
 8-hydroxymethyl-1-isopropenylnaphthalene;
 methoxymethyl-1-vinylnaphthalene compounds such as
 25 4-methoxymethyl-1-vinylnaphthalene,
 7-methoxymethyl-1-vinylnaphthalene,
 8-methoxymethyl-1-vinylnaphthalene,

4-methoxymethyl-1-isopropenylnaphthalene,
7-methoxymethyl-1-isopropenylnaphthalene, and
8-methoxymethyl-1-isopropenylnaphthalene; and other
vinylnaphthalene compounds such as

- 5 4-phenoxyethyl-1-vinylnaphthalene,
4-vinyloxyethyl-1-vinylnaphthalene,
4-acetoxyethyl-1-vinylnaphthalene,
4-phenoxyethyl-1-isopropenylnaphthalene,
4-vinyloxyethyl-1-isopropenylnaphthalene,
10 4-acetoxyethyl-1-isopropenylnaphthalene.

Of these aromatic vinyl compounds,
4-hydroxyethylstyrene, 4-methoxyethylstyrene,
2-hydroxyethyl-6-vinylnaphthalene, and the like are
particularly preferable.

- 15 These aromatic vinyl compounds may be used either
individually or in combination of two or more.

- The compounds previously given in the description
relating to other copolymerizable unsaturated compounds in the
polymer (I) can be given as examples of other copolymerizable
20 unsaturated compounds in the polymer (II) used here.

Of such other copolymerizable unsaturated compounds,
styrene is particularly preferable.

These other copolymerizable unsaturated compounds may
be used either individually or in combination of two or more.

- 25 The amount of the structural unit derived from these other
copolymerizable unsaturated compounds in the polymer (II) is
preferably 80 mol% or less, more preferably 60 mol% or less,

and particularly preferably 40 mol% or less of the total amount of the structural units.

Mw of the polymer (II) is suitably selected according to desired characteristics of the antireflection film, usually
5 in the range of 500-10,000, and preferably 1,000-5,000.

Polymers (III) to (V)

The structural unit (3) of the polymer (I) is used as the structural unit (3) in the polymer (III) and polymer (IV). The structural unit (4) of the polymer (II) is used as the
10 structural unit (4) in the polymer (IV) and polymer (V).

As examples of the monovalent atom or monovalent organic group represented by R^6 or R^7 in the structural unit (5), the same monovalent atoms or monovalent groups as those previously given for the groups R^2 and R^3 in the structural unit (3) can
15 be given.

A hydrogen atom, methyl group, and the like are particularly preferable for R^6 and R^7 in the structural unit (5).

The polymer (III) can be prepared by polymerizing an
20 acenaphthylene corresponding to the structural unit (3) and an aromatic vinyl compound corresponding to the structural unit (4), optionally together with another copolymerizable unsaturated monomer. The polymer (IV) can be prepared by polymerizing an acenaphthylene corresponding to the structural
25 unit (3) and an acenaphthylene compound corresponding to the structural unit (5), optionally together with another copolymerizable unsaturated monomer. The polymer (V) can be

prepared by polymerizing an aromatic vinyl compound corresponding to the structural unit (4) and an acenaphthylene corresponding to the structural unit (5), optionally together with another copolymerizable unsaturated monomer.

5 Radical polymerization, anionic polymerization, cationic polymerization, or the like using an appropriate process such as mass polymerization process, solution polymerization process, or the like can be used for manufacturing the polymers (III) to (V).

10 The polymer (III) having the structural unit (3) in which the R^1 group is a hydrogen atom or the structural unit (4) in which the R^4 group is a hydrogen atom, the polymer (IV) having the structural unit (3) in which the R^1 group is a hydrogen atom, and the polymer (V) having the structural unit (4) in which the
15 R^4 group is a hydrogen atom can be respectively produced by hydrolyzing the acetoxymethyl group of the polymers (III), (IV), and (V) having the acetoxymethyl group by a conventional method. The polymer (III) having the structural unit (3) in which the R^1 group is an acetyl group or the structural unit (4) in which
20 the R^4 group is an acetyl group, the polymer (IV) having the structural unit (3) in which the R^1 group is an acetyl group, and the polymer (V) having the structural unit (4) in which the R^4 group is an acetyl group can be respectively produced by acetylating the hydroxyl group of the polymers (III), (IV), and
25 (V) having the hydroxyl group by a conventional method.

 The compounds previously given in the description relating to the acenaphthylene corresponding to the structural

unit (3) in the polymer (I) can be given as examples of the acenaphthylenes corresponding to the structural unit (3) in the polymers (III) and (IV) used here. Of these acenaphthylenes, 3-hydroxymethylacenaphthylene,
5 4-hydroxymethylacenaphthylene,
5-hydroxymethylacenaphthylene,
3-methoxymethylacenaphthylene,
4-methoxymethylacenaphthylene, and
5-methoxymethylacenaphthylene are particularly preferable.

10 These acenaphthylenes may be used either individually or in combinations of two or more.

 The compounds previously given in the description relating to the aromatic vinyl compounds corresponding to the structural unit (4) in the polymer (II) can be given as examples
15 of the aromatic vinyl compound corresponding to the structural unit (4) in the polymers (III) and (V) used here.

 Of these aromatic vinyl compounds,
4-hydroxymethylstyrene, 4-methoxymethylstyrene, and the like are particularly preferable.

20 These aromatic vinyl compounds may be used either individually or in combination of two or more.

 As examples of the preferable acenaphthylene corresponding to the structural unit (5) in the polymers (IV) and (V), acenaphthylene, 1-methylacenaphthylene,
25 1,2-dimethylacenaphthylene, 1-phenylacenaphthylene,
1,2-diphenylacenaphthylene, and
1-methyl-2-phenylacenaphthylene can be given.

Of these acenaphthylenes, acenaphthylene is particularly preferable.

These acenaphthylenes may be used either individually or in combinations of two or more.

5 The compounds previously given in the description relating to other copolymerizable unsaturated compounds in the polymer (I) can be given as other copolymerizable unsaturated compounds in the polymers (III), (IV), and (V) used here, for example.

10 These other copolymerizable unsaturated compounds may be used either individually or in combination of two or more.

 In the polymer (III), the content of the structural unit (3) is preferably 5-80 mol%, more preferably 10-60 mol%, and particularly preferably 10-40 mol% of the total amount of the structural units, the content of the structural unit (4) is
15 preferably 5-80 mol%, more preferably 5-60 mol%, and particularly preferably 5-40 mol%, and the content of the structural unit derived from other copolymerizable unsaturated compounds is 50 mol% or less, and more preferably 30 mol% or
20 less.

 In the polymer (IV), the content of the structural unit (3) is preferably 5-80 mol%, more preferably 10-60 mol%, and particularly preferably 10-40 mol% of the total amount of the structural units, the content of the structural unit (5) is
25 preferably 5-95 mol%, more preferably 10-90 mol%, and particularly preferably 20-90 mol%, and the content of the structural unit derived from other copolymerizable unsaturated

compounds is 50 mol% or less, and more preferably 30 mol% or less.

In the polymer (V), the content of the structural unit (4) is preferably 5-80 mol%, more preferably 10-60 mol%, and particularly preferably 15-60 mol% of the total amount of the structural units, the content of the structural unit (5) is preferably 5-95 mol%, more preferably 10-90 mol%, and particularly preferably 20-80 mol%, and the content of the structural unit derived from other copolymerizable unsaturated compounds is 50 mol% or less, and more preferably 30 mol% or less.

Mw of the polymers (III), (IV), and (V) is suitably selected according to desired characteristics of the antireflection film, usually in the range of 500-10,000, and preferably 500-5,000.

Solvent

Any solvent capable of dissolving the above-described polymers and later-described additives can be used for preparing the antireflection film-forming composition of the present invention without any specific limitation. Examples of the solvent that can be suitably selected include: ethylene glycol monoalkyl ethers such as ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, ethylene glycol mono-n-propyl ether, and ethylene glycol mono-n-butyl ether; ethylene glycol monoalkyl ether acetates such as ethylene glycol monomethyl ether acetate, ethylene glycol monoethyl

ether acetate, ethylene glycol mono-n-propyl ether acetate, and ethylene glycol mono-n-butyl ether acetate; diethylene glycol dialkyl ethers such as diethylene glycol dimethyl ether, diethylene glycol diethyl ether, diethylene glycol di-n-propyl ether, diethylene glycol di-n-butyl ether; 5 triethylene glycol dialkyl ethers such as triethylene glycol dimethyl ether and triethylene glycol diethyl ether; propylene glycol monoalkyl ethers such as propylene glycol monomethyl ether, propylene glycol monoethyl ether, propylene glycol mono-n-propyl ether, and propylene glycol mono-n-butyl ether; propylene glycol dialkyl ethers such as propylene glycol dimethyl ether, propylene glycol diethyl ether, propylene glycol di-n-propyl ether, and propylene glycol di-n-butyl ether; propylene glycol monoalkyl ether acetates such as 15 propylene glycol monomethyl ether acetate, propylene glycol monoethyl ether acetate, propylene glycol mono-n-propyl ether acetate, and propylene glycol mono-n-butyl ether acetate; lactic acid esters such as methyl lactate, ethyl lactate, n-propyl lactate, i-propyl lactate, n-butyl lactate, and i-butyl lactate; 20 aliphatic carboxylic acid esters such as methyl formate, ethyl formate, n-propyl formate, i-propyl formate, n-butyl formate, i-butyl formate, n-amyl formate, i-amyl formate, methyl acetate, ethyl acetate, n-propyl acetate, i-propyl acetate, n-butyl acetate, i-butyl acetate, n-amyl acetate, i-amyl acetate, n-hexyl acetate, methyl propionate, ethyl propionate, n-propyl propionate, i-propyl propionate, 25 n-butyl propionate, i-butyl propionate, methyl butyrate, ethyl

butyrate, n-propyl butyrate, i-propyl butyrate, n-butyl butyrate, and i-butyl butyrate; other esters such as ethyl hydroxyacetate, ethyl 2-hydroxy-2-methylpropionate, methyl 3-methoxy-2-methylpropionate, methyl
5 2-hydroxy-3-methylbutyrate, ethyl methoxyacetate, ethyl ethoxyacetate, methyl 3-methoxypropionate, ethyl 3-ethoxypropionate, ethyl 3-methoxypropionate, 3-methoxypropyl acetate, 3-methoxybutyl acetate, 3-methyl-3-methoxybutyl acetate, 3-methyl-3-methoxybutyl
10 propionate, 3-methyl-3-methoxybutyl butyrate, methyl acetoacetate, methyl pyruvate, and ethyl pyruvate; aromatic hydrocarbons such as toluene and xylene; ketones such as methyl ethyl ketone, methyl n-propyl ketone, methyl n-butyl ketone, 2-heptanone, 3-heptanone, 4-heptanone,
15 and cyclohexanone; amides such as N-methylformamide, N,N-dimethylformamide, N-methylacetamide, N,N-dimethyl acetamide, and N-methylpyrrolidone; and lactones such as γ -butyrolactone.

Of these solvents, ethylene glycol monoethyl ether
20 acetate, ethyl lactate, n-butyl acetate, ethyl 3-ethoxypropionate, methyl 3-methoxypropionate, 2-heptanone, cyclohexanone, and the like are preferable. These solvents may be used either individually or in combination of two or more. The solvent is used in an amount to make the solid content in
25 the resulting composition usually 0.01-70 wt%, preferably 0.05-60 wt%, and more preferably 0.1-50 wt%.

Additives

Additives such as an acid generator, crosslinking agent, binder resin, radiation absorbent, and surfactant may be optionally added to the antireflection film-forming composition of the present invention to the extent not impairing the effect of the present invention. The addition of an acid generator and/or crosslinking agent is particularly preferable.

The acid generator is a component that generates an acid upon exposure to light or when heated.

The following compounds can be given as examples of the acid generator that generates an acid upon exposure to light (hereinafter referred to as "photoacid generator"): onium salt photoacid generators such as diphenyliodonium trifluoromethanesulfonate, diphenyliodonium nonafluoro-n-butanesulfonate, diphenyliodonium pyrenesulfonate, diphenyliodonium n-dodecylbenzenesulfonate, diphenyliodonium 10-camphorsulfonate, diphenyliodonium naphthalenesulfonate, diphenyliodonium hexafluoroantimonate, bis(4-t-butylphenyl)iodonium trifluoromethanesulfonate, bis(4-t-butylphenyl)iodonium nonafluoro-n-butanesulfonate, bis(4-t-butylphenyl)iodonium n-dodecylbenzenesulfonate, bis(4-t-butylphenyl)iodonium 10-camphorsulfonate, bis(4-t-butylphenyl)iodonium naphthalenesulfonate, bis(4-t-butylphenyl)iodonium hexafluoroantimonate, triphenylsulfonium trifluoromethanesulfonate, triphenylsulfonium nonafluoro-n-butanesulfonate,

triphenylsulfonium n-dodecylbenzenesulfonate,
triphenylsulfonium naphthalenesulfonate, triphenylsulfonium
10-camphorsulfonate, triphenylsulfonium
hexafluoroantimonate,

5 4-hydroxyphenyl·phenyl·methylsulfonium p-toluenesulfonate,
4-hydroxyphenyl·benzyl·methylsulfonium p-toluenesulfonate,
cyclohexyl·methyl·2-oxocyclohexylsulfonium
trifluoromethanesulfonate,
2-oxocyclohexyldicyclohexylsulfonium

10 trifluoromethanesulfonate, 2-oxocyclohexyldimethylsulfonium
trifluoromethanesulfonate,
1-naphthyldimethylsulfonium trifluoromethanesulfonate,
1-naphthyldiethylsulfonium trifluoromethanesulfonate,
4-cyano-1-naphthyldimethylsulfonium

15 trifluoromethanesulfonate,
4-cyano-1-naphthyldimethylsulfonium
trifluoromethanesulfonate,
4-nitro-1-naphthyldimethylsulfonium
trifluoromethanesulfonate,

20 4-nitro-1-naphthyldiethylsulfonium
trifluoromethanesulfonate,
4-methyl-1-naphthyldimethylsulfonium
trifluoromethanesulfonate,
4-methyl-1-naphthyldiethylsulfonium

25 trifluoromethanesulfonate,
4-hydroxy-1-naphthyldimethylsulfonium
trifluoromethanesulfonate,

- 4-hydroxy-1-naphthyl-diethylsulfonium
trifluoromethanesulfonate,
1-(4-hydroxynaphthalen-1-yl)tetrahydrothiophenium
trifluoromethanesulfonate,
- 5 1-(4-methoxynaphthalen-1-yl)tetrahydrothiophenium
trifluoromethanesulfonate,
1-(4-ethoxynaphthalen-1-yl)tetrahydrothiophenium
trifluoromethanesulfonate,
1-(4-methoxymethoxynaphthalen-1-yl)tetrahydrothiophenium
- 10 trifluoromethanesulfonate,
1-(4-ethoxymethoxynaphthalen-1-yl)tetrahydrothiophenium
trifluoromethanesulfonate,
1-[4-(1-methoxyethoxy)naphthalen-1-yl]tetrahydrothiophenium
trifluoromethanesulfonate,
- 15 1-[4-(2-methoxyethoxy)naphthalen-1-yl]tetrahydrothiophenium
trifluoromethanesulfonate,
1-(4-methoxycarbonyloxynaphthalen-1-yl)tetrahydrothiophenium
trifluoromethanesulfonate,
1-(4-ethoxycarbonyloxynaphthalen-1-yl)tetrahydrothiophenium
- 20 trifluoromethanesulfonate,
1-(4-n-propoxycarbonyloxynaphthalen-1-yl)-
tetrahydrothiophenium trifluoromethanesulfonate,
1-(4-i-propoxycarbonyloxynaphthalen-1-yl)-
tetrahydrothiophenium trifluoromethanesulfonate,
- 25 1-(4-n-butoxycarbonyloxynaphthalen-1-yl)-
tetrahydrothiophenium trifluoromethanesulfonate,
1-(4-t-butoxycarbonyloxynaphthalen-1-yl)-

tetrahydrothiophenium trifluoromethanesulfonate,
 1-[4-(2-tetrahydrofuranyloxy)naphthalen-1-yl]-
 tetrahydrothiophenium trifluoromethanesulfonate,
 1-[4-(2-tetrahydropyranyloxy)naphthalen-1-yl]-
 5 tetrahydrothiophenium trifluoromethanesulfonate,
 1-(4-benzyloxy)tetrahydrothiophenium
 trifluoromethanesulfonate,
 and 1-(naphthylacetomethyl)tetrahydrothiophenium
 trifluoromethanesulfonate;
 10 halogen-containing photoacid generators such as
 phenylbis(trichloromethyl)-s-triazine,
 4-methoxyphenylbis(trichloromethyl)-s-triazine, and
 1-naphthylbis(trichloromethyl)-s-triazine;
 diazoketone compound photoacid generators such as
 15 1,2-naphthoquinonediazido-4-sulfonyl chloride,
 1,2-naphthoquinonediazido-5-sulfonyl chloride,
 1,2-naphthoquinonediazido-4-sulfonate or
 1,2-naphthoquinonediazido-5-sulfonate of
 2,3,4,4'-tetrahydroxybenzophenone;
 20 sulfone compound photoacid generators such as
 4-trisphenacylsulfone, mesitylphenacylsulfone, and
 bis(phenylsulfonyl)methane; and
 sulfonate compound photoacid generators such as
 benzointosylate, pyrogallol tris(trifluoromethanesulfonate),
 25 nitrobenzyl-9,10-diethoxyanthracene-2-sulfonate,
 trifluoromethanesulfonylbicyclo[2,2,1]hept-5-ene-2,3-dicarb
 odiimide, N-hydroxysuccinimido trifluoromethanesulfonate,

and 1,8-naphthalenedicarboxylic acid imide
trifluoromethanesulfonate.

Of these photoacid generators, diphenyliodonium
trifluoromethanesulfonate, diphenyliodonium
5 nonafluoro-n-butanesulfonate, diphenyliodonium
pyrenesulfonate, diphenyliodonium n-dodecylbenzenesulfonate,
diphenyliodonium 10-camphorsulfonate, diphenyliodonium
naphthalenesulfonate, bis(4-t-butylphenyl)iodonium
trifluoromethanesulfonate, bis(4-t-butylphenyl)iodonium
10 nonafluoro-n-butanesulfonate, bis(4-t-butylphenyl)iodonium
n-dodecylbenzenesulfonate, bis(4-t-butylphenyl)iodonium
10-camphorsulfonate, bis(4-t-butylphenyl)iodonium
naphthalenesulfonate, and the like are preferable.

The photoacid generators may be used either individually
15 or in combination of two or more.

As the acid generators generating an acid when heated
(hereinafter referred to as "heat acid generator"),
2,4,4,6-tetrabromocyclohexadienone, benzointosylate,
2-nitrobenzyltosylate, alkyl sulfonates, and the like can be
20 given.

These heat acid generators may be used either
individually or in combination of two or more.

The photoacid generator and heat acid generator may be
used in combination. The amount of acid generators to be added
25 is usually 5,000 parts by weight or less, preferably 0.1-1,000
parts by weight, and particularly preferably 0.1-100 parts by
weight for 100 parts by weight of the solid content of the

antireflection film-forming composition. The addition of a photoacid generator and/or a heat acid generator to the antireflection film-forming composition of the present invention ensures the molecular chains in the polymers to
5 effectively crosslink at a relatively low temperature, including a room temperature.

The crosslinking agent is a component effective for preventing intermixing between the resulting antireflection film and a resist coating produced thereon and also preventing
10 cracks in the antireflection film.

Polynuclear phenolic compounds and various commercially available curing agents can be used as such a crosslinking agent.

As examples of the polynuclear phenolic compound,
15 binuclear phenols such as 4,4'-biphenyldiol, 4,4'-methylenebisphenol, 4,4'-ethylidenebisphenol, and bisphenol A; trinuclear phenols such as 4,4',4''-methylenetrisphenol, and 4,4'-[1-{4-(1-[4-hydroxyphenyl]-1-methylethyl)phenyl}-ethylidene]bisphenol; and polyphenols such as novolaks can be
20 given.

Of these polynuclear phenolic compounds, 4,4'-[1-{4-(1-[4-hydroxyphenyl]-1-methylethyl)phenyl}-ethylidene]bisphenol, novolaks, and the like are preferable.

25 These polynuclear phenolic compounds may be used either individually or in combination of two or more.

As curing agents, diisocyanates such as 2,3-tolylene

diisocyanate, 2,4-tolylene diisocyanate, 3,4-tolylene diisocyanate, 3,5-tolylene diisocyanate, 4,4'-diphenylmethane diisocyanate, hexamethylene diisocyanate, and 1,4-cyclohexane diisocyanate; commercially available products such as epoxy compounds, such as Epikoto 812, 815, 826, 828, 834, 836, 871, 1001, 1004, 1007, 1009, 1031 (manufactured by Japan Epoxy Resins Co., Ltd.); Araldite 6600, 6700, 6800, 502, 6071, 6084, 6097, 6099 (manufactured by Ciba Specialty Chemicals Inc.); DER331, 332, 333, 661, 644, 667 (manufactured by Dow Chemical Company); melamine-type curing agents such as Cymel 300, 301, 303, 350, 370, 771, 325, 327, 703, 712, 701, 272, 202, Mycoat 506, 508 (manufactured by Mitsui Cyanamid); benzoquanamine-type curing agents such as Cymel 1123, 1123-10, 1128, Mycoat 102, 105, 106, 130 (manufactured by Mitsui Cytec, Ltd.); and glycoluril-type curing agents such as Cymel 1170, 1172 (manufactured by Mitsui Cytec, Ltd.) and NIKALAC N-2702 (manufactured by Sanwa Chemical Co., Ltd.); and the like can be given.

Of these curing agents, melamine-type curing agents, glycoluril-type curing agents, and the like are preferable.

These curing agents may be used either individually or in combination of two or more.

In addition, the polynuclear phenolic compound and curing agent can be used in combination as crosslinking agent. The amount of crosslinking agents to be added is usually 5,000 parts by weight or less, and preferably 1,000 parts by weight or less, for 100 parts by weight of the solid content of the

antireflection film-forming composition.

As the above binder resins, various thermoplastic resins and thermoset (or heat curable) resins can be used.

Given as examples of the thermoplastic resins are:

- 5 α -olefin polymers such as polyethylene, polypropylene, poly-1-butene, poly-1-pentene, poly-1-hexene, poly-1-heptene, poly-1-octene, poly-1-decene, poly-1-dodecene, poly-1-tetradecene, poly-1-hexadecene, poly-1-octadecene, and polyvinylcycloalkane; non-conjugated diene polymers such
- 10 as poly(1,4-pentadiene), poly(1,4-hexadiene), and poly(1,5-hexadiene); α,β -unsaturated aldehyde polymers; α,β -unsaturated ketone polymers such as poly(methyl vinyl ketone), poly(aromatic vinyl ketone) and poly(cyclic vinyl ketone); polymers of α,β -unsaturated carboxylic acids or their
- 15 derivatives such as (meth)acrylic acid, α -chloroacrylic acid, (meth)acrylic acid salts, (meth)acrylic acid esters, (meth)acrylic acid halides, and the like; polymers of α,β -unsaturated carboxylic acid anhydrides such as poly(meth)acrylic acid anhydride and copolymers of maleic acid
- 20 anhydride; polymers of unsaturated polybasic carboxylic acid esters such as methylene malonic acid diester and itaconic acid diester; polymers of diolefin carboxylic acid esters such as sorbic acid ester and muconic acid ester; polymers of α,β -unsaturated carboxylic acid thioesters such as
- 25 (meth)acrylic acid thioester and α -chloroacrylic acid thioester; polymers of (meth)acrylonitrile or its derivatives such as (meth)acrylonitrile and α -chloroacrylonitrile;

polymers of (meth)acrylamide or its derivatives such as (meth)acrylamide and N,N-dimethyl(meth)acrylamide; polymers of styryl metallic compounds; polymers of vinyloxy metallic compounds; polyimines; polyethers such as polyphenylene oxide, poly(1,3-dioxolane), polyoxirane, polytetrahydrofuran, and polytetrahydropyrane; polysulfides; polysulfonamides; polypeptides; polyamides such as Nylon 66 and Nylons 1 to 12; polyesters such as aliphatic polyester, aromatic polyester, alicyclic polyester, and polycarbonate; polyureas; polysulfones; polyazines; polyamines; polyaromatic ketones; polyimides; polybenzoimidazoles; polybenzoxazoles; polybenzothiazoles; polyaminotriazoles; polyoxadiazoles; polypyrazoles; polytetrazoles; polyquinoxalines; polytriazines; polybenzoxazinones; polyquinolines; and anthrazolines.

The heat curable resins are components becoming insoluble in solvents by curing with heat and preventing intermixing between the resulting antireflection film and a resist coating formed thereon. The resins can be preferably used as the binder resins.

As examples of such a heat-curable resin, heat-curable acrylic resins, phenol resins, urea resins, melamine resins, amino-type resins, aromatic hydrocarbon resins, epoxy resins, and alkyd resins can be given.

Of these heat curable resins, urea resins, melamine resins, aromatic hydrocarbon resins, and the like are preferable.

The above binder resins may be used either individually or in combination of two or more.

The amount of binder resin to be added is usually 20 parts by weight or less, and preferably 10 parts by weight or less,
5 for 100 parts by weight of the polymers in the antireflection film-forming composition.

As the radiation absorbers, dyes such as oil soluble dyes, disperse dyes, basic dyes, methine-type dyes, pyrazole-type dyes, imidazole-type dyes, and hydroxyazo-type dyes;
10 fluorescent brightening agents such as bixin derivatives, norbixin, stilbene, 4,4'-diaminostilbene derivatives, coumarin derivatives, and pyrazoline derivatives; UV absorbers such as hydroxyazo-type dyes, Tinuvin 234 (manufactured by Ciba Specialty Chemicals, Inc.), and Tinuvin 1130 (manufactured by
15 Ciba Specialty Chemicals, Inc.); aromatic compounds such as anthracene derivatives and anthraquinone derivatives; and the like can be given.

These radiation absorbers may be used either individually or in combination of two or more.

20 The amount of radiation absorber to be added is usually 100 parts by weight or less, and preferably 50 parts by weight or less, for 100 parts by weight of the solid content of the antireflection film-forming composition.

The surfactants are components exhibiting the effects
25 of improving applicability, striation, wettability, and developability.

As the surfactants, nonionic surfactants such as

polyoxyethylene lauryl ether, polyoxyethylene stearyl ether, polyoxyethylene oleyl ether, polyoxyethylene n-octyl phenyl ether, polyoxyethylene n-nonyl phenyl ether, polyethylene glycol dilaurate, and polyethylene glycol distearate;

5 commercially available products such as KP341 (manufactured by Shin-Etsu Chemical Co., Ltd.), Polyflow No. 75, No. 95 (manufactured by Kyoeisha Chemical Co., Ltd.), FFTOP EF101, EF204, EF303, EF352 (manufactured by JEMCO, Inc.), MEGAFACE F171, F172, F173 (manufactured by Dainippon Ink and Chemicals, Inc.), Fluorad FC430, FC431, FC135, FC93 (manufactured by
10 Sumitomo 3M Ltd.), Asahi Guard AG710, Surflon S382, SC101, SC102, SC103, SC104, SC105, SC106 (manufactured by Asahi Glass Co., Ltd.), and the like can be given.

The surfactants may be used either individually or in
15 combination of two or more.

The amount of surfactant to be added is usually 15 parts by weight or less, and preferably 10 parts by weight or less, for 100 parts by weight of the solid content of the antireflection film-forming composition.

20 As other additives, storage stabilizers, anti-foaming agents, adhesion adjuvants, and the like can be given.

Process for forming antireflection film

The process for forming an antireflection film from the
25 antireflection film-forming composition (hereinafter referred to as "composition") of the present invention comprises, for example, 1) a step of forming an antireflection film on a

substrate by applying the composition onto a substrate and curing the coating, 2) a step of forming a resist film by applying a resist composition solution onto the antireflection film and prebaking the applied coating, 3) a step of exposing selected
5 areas of the resist coating to radiation through a photomask, 4) a step of developing the exposed resist coating, and 5) a step of etching the antireflection film.

A silicon wafer or a wafer coated with aluminum, for example, can be used as the substrate in step 1). The composition
10 is coated by an appropriate method such as rotation application, cast coating, and roll application.

The coating film is cured by radiation and/or heat. The type of radiation used for exposure is appropriately selected according to the type of photoacid generator from among visible
15 radiation, ultraviolet radiation, deep ultraviolet rays, X-rays, electron beams, γ -rays, molecular beams, ion beams, and the like. When the composition containing a photoacid generator is exposed to light, the coating film can be effectively cured at a room temperature. Usually, the heating
20 temperature is about 90-350°C, and preferably about 200-300°C. However, when the composition contains a photoacid generator, the coating film can be effectively cured at about 90-150°C, for example.

The thickness of the antireflection film formed in step
25 1) is usually 0.1-5 μm .

Next, in step 2), the resist film having a specific thickness is formed by applying the resist composition solution

on the antireflection film so that the resulting resist film may have a prescribed thickness and by prebaking the resulting coating to volatilize the solvent. In this instance, the prebaking temperature is appropriately adjusted according to
5 the type of resist composition in the range usually of 30-200°C, and preferably of 50-150°C.

As the resist composition, a chemically amplified positive tone or negative tone resist composition containing a photoacid generator, a positive tone resist composition
10 comprising an alkali-soluble resin and a quinone diazido sensitizer, a negative tone resist composition comprising an alkali-soluble resin and a crosslinking agent, and the like can be given.

The resist composition solution used for forming a resist
15 film on the antireflection film has a solid component content usually of about 5-50 wt% and is used for resist film formation after filtering through a filter with a pore diameter of about 0.2 μm . A commercially available resist composition solution can be used as is in this step.

20 Radiation used for exposure in step 3) is appropriately selected according to the type of photoacid generator used in the resist composition from among visible rays, ultraviolet rays, deep ultraviolet rays, X-rays, electron beams, γ -rays, molecular beams, ion beams, and the like. Of these radiations,
25 deep ultraviolet rays, particularly a KrF excimer laser (wavelength: 248 nm), ArF excimer laser (wavelength: 193 nm), F₂ excimer laser (wavelength: 157 nm), Kr₂ excimer laser

(wavelength: 147 nm), ArKr excimer laser (wavelength: 134 nm), and extreme ultraviolet rays (wavelength: 13 nm) are preferable.

Next, in step 4), the resist film after exposure is developed, washed, and dried to form a target resist pattern. In this step, postbaking may be carried out after exposure and before development to improve resolution, pattern profile, developability, and the like.

The developer used in this step is appropriately selected from the type of resist composition used. As examples of the developer used for a chemically amplified positive tone resist composition or a positive tone resist composition containing an alkali-soluble resin, alkaline aqueous solutions prepared by dissolving alkaline compounds such as sodium hydroxide, potassium hydroxide, sodium carbonate, sodium silicate, sodium metasilicate, aqueous ammonia, ethylamine, n-propylamine, diethylamine, di-n-propylamine, triethylamine, methyldiethylamine, dimethylethanolamine, triethanolamine, tetramethylammonium hydroxide, tetraethylammonium hydroxide, pyrrole, piperidine, choline, 1,8-diazabicyclo-[5.4.0]-7-undecene, and 1,5-diazabicyclo-[4.3.0]-5-nonene can be given. An appropriate amount of a water-soluble organic solvent such as alcohols including methanol and ethanol or a surfactant can be added to these alkaline aqueous solutions.

Next, in step 5), the antireflection film is etched by dry etching using the obtained resist pattern as a mask and a

gas plasma such as oxygen plasma to obtain a desired resist pattern for substrate processing.

EXAMPLES

5 The present invention is described below in more detail by examples. However, these examples should not be construed as limiting the present invention. In the examples, part(s) and % refer to part(s) by weight and wt% unless otherwise indicated.

10

Example 1 (synthesis of acenaphthylene derivative)

Step 1

15 150 g of tin chloride was added dropwise to a solution of dichloromethyl methyl ether (70 g) in dichloroethane (300 g) while stirring at -5°C under a dry atmosphere. Then, a solution of acenaphthene (77 g) in dichloroethane (300 g) was added. After stirring for two hours at room temperature, an aqueous solution of 5% calcium chloride was slowly added to the reaction solution. The organic phase was washed until the water
20 phase becomes neutral and then removed. The solvent was evaporated to obtain 90.5 g of a pale yellow solid compound.

¹H-NMR spectrum (solvent: deuterium chloroform, hereinafter the same) and IR spectrum were measured to identify the compound to be formyl acenaphthene. The measurement results
25 were as follows.

σ (unit ppm): 3.4 (CH₂ group)

7.3-8.8, 10.5 (CHO group)

IR (unit cm^{-1}): 1677 (C=O group)

Step 2

Formyl acenaphthene (73 g) obtained in Step 1 was
5 dissolved in a mixed solvent of tetrahydrofuran and ethanol
(tetrahydrofuran: 550 g, ethanol: 110 g). Sodium borohydride
(7.6 g) was added to the solution and the mixture was stirred
for two hours at room temperature. The reaction solution was
concentrated and water was added to the residue to collect a
10 deposited compound by filtration. The filtrate was dried under
reduced pressure to obtain 71 g of white solid.

^1H -NMR spectrum (δ) and IR spectrum were measured to
identify the compound to be hydroxymethylacenaphthene. The
measurement results were as follows.

15 σ (unit ppm): 3.3 (CH_2 group)
4.8-4.9 ($\text{CH}_2\text{-O}$ group)
5.2-5.3 (OH group)
7.2-7.8 (hydrogen atom of aromatic ring)

IR (unit cm^{-1}): 3372, 3297 (OH groups)

20 Step 3

Hydroxymethylacenaphthene (55 g) obtained in Step 2 was
dissolved in dioxane (1,200 g). Acetyl chloride (26 g) and
triethylamine (36 g) were added to the solution in this order
while maintaining the temperature to 50°C or less. The mixture
25 was stirred for three hours at 90°C. Insoluble components were
separated by filtration. The organic phase was concentrated
and the solvent was replaced with toluene. The toluene solution

was washed until the water phase becomes neutral. The solvent was evaporated to obtain 65 g of a yellow solid compound.

¹H-NMR spectrum (δ) and IR spectrum were measured to identify the compound to be acetoxymethylacenaphthene. The measurement results were as follows.

σ (unit ppm): 2.1 (CH₃ group)

3.3-3.4 (CH₂ group)

5.5 (CH₂-O group)

7.2-7.5 (hydrogen atom of aromatic ring)

IR (unit cm⁻¹): 1725 (C=O group)

Step 4

The acetoxymethylacenaphthene (45 g) obtained in Step 3 was dissolved in dioxane (450 g). After the addition of dichlorodicyanobenzoquinone (60 g), the mixture was stirred for seven hours at 95°C. The reaction mixture was filtered and the solvent was evaporated from the filtrate to obtain 54 g of acetoxymethylacenaphthylene as a brown solid.

Step 5

Acetoxymethylacenaphthylene (44 g) was dissolved in methanol (300 g). After the addition of 10% NaOH aqueous solution (110 g) dropwise, the mixture was stirred for two hours at 60°C. Methanol was evaporated from the reaction solution to replace the solvent with methyl ethyl ketone (350 g). The methyl ethyl ketone solution was washed until the water phase becomes neutral. The solvent was evaporated to obtain a yellow solid compound. The yellow solid compound was purified by recrystallization to obtain 10 g of a compound.

^1H -NMR spectrum (δ) and IR spectrum were measured to identify the compound to be hydroxymethylacenaphthylene. The measurement results were as follows.

σ (unit ppm): 5.1 ($\text{CH}_2\text{-O}$ group)

5 5.4 (OH group)

7.2 (HC=CH group)

7.6-8.2 (hydrogen atom of aromatic ring)

IR (unit cm^{-1}): 3423 (OH group)

Synthesis Example 1

10 (Synthesis of 2-hydroxymethyl-6-vinylnaphthalene)

Methyl 6-bromo-2-naphthalene carboxylate (98 g) was dissolved in dimethoxyethane (2 l) and tetrakis(triphenylphosphine)palladium (44 g) was added in nitrogen atmosphere. The mixture was stirred for 30 minutes
15 at room temperature. Potassium carbonate (52 g), water (1 l), and 2,4,6-trivinylcyclotriboroxane-pyridine complex (91 g) were added and the mixture was stirred for 24 hours while refluxing with heating. The reaction mixture was cooled to room temperature and treated with activated alumina to obtain methyl
20 2-vinyl-6-naphthalene carboxylate (77 g).

The methyl 2-vinyl-6-naphthalene carboxylate (30 g) was dissolved in tetrahydrofuran and 1 M diisobutylaluminum hydride (DIBAL-H) solution (400 ml) was added at -78°C . After confirming completion of the reaction with thin layer
25 chromatography, the reaction mixture was treated with methanol and water, and extracted with ethyl acetate.

The organic layer was washed with brine, dried over

anhydrous sodium sulfate, filtered, and concentrated.

The residue was purified by silica gel column chromatography to obtain a compound (18.5 g).

¹H-NMR spectrum (δ) shown below identified that the
5 compound was 2-hydroxymethyl-6-vinylnaphthalene.

σ (unit ppm): 4.9 (CH₂-O group)

5.3, 5.9, 6.9 (vinyl group),

7.6-7.8 (hydrogen atom on aromatic ring)

10 In the following Preparation Example 1 and Examples 2-3,
Mw of the obtained polymers was measured by gel permeation
chromatography (detector: differential refractometer) using
GPC columns (manufactured by Tosoh Corp., G2000H^{XL} x 2, G3000H^{XL}
x 1) under the following conditions. Flow rate: 1.0 ml/minute,
15 eluate: tetrahydrofuran, column temperature: 40°C, reference
material: monodispersed polystyrene.

Performance of antireflection film-forming compositions
was evaluated as follows.

<Optical characteristics>

20 The antireflection film-forming composition was
spincoated on a silicon wafer with a diameter of eight inches
and heated for 120 seconds on a hot plate at 345°C to obtain
an antireflection film with a thickness of 1 μm. Refractive
index (n value) and absorbance (k value) of the antireflection
25 film were measured at a wavelength of 248 nm using a
spectroscopic Ellipsometer UV-1280E (manufactured by
KLA-TENCOR Corp.). The n value and k value were also measured

at a wavelength of 193 nm using a spectroscopic Ellipsometer MOSS-ESVG DEEP UV (manufactured by SOPRA Inc.).

<Formation of positive type resist pattern for KrF>

The antireflection film-forming composition was spin
5 coated on a silicon wafer with a diameter of 8 inch and heated
for 120 seconds on a hot plate at 345°C to obtain an
antireflection film with a thickness of 0.6 μm . A resist
composition solution for KrF (KRFM 20G, manufactured by JSR
Corporation) was spin coated onto the antireflection film and
10 prebaked for 60 seconds on a hot plate at 140°C to obtain a resist
film with a thickness of 0.61 μm . The resist film was exposed
to a KrF excimer laser using a stepper NSR2205 EX12B
(wavelength: 248 nm, manufactured by Nikon Corp.) through a mask
at an optimal dose for producing a 1:1 line-and-space pattern
15 with a line width of 0.22 μm . After postbaking on a hot plate
at 140°C for 90 seconds, the resist film was developed using
a 2.38 wt% tetramethylammonium hydroxide aqueous solution at
23°C for 30 minute, washed with water, and dried to form a
positive-tone resist pattern.

20 <Formation of positive type resist pattern for ArF>

The antireflection film-forming composition was spin
coated on a silicon wafer with a diameter of eight inches and
baked for 120 seconds on a hot plate at 345°C to obtain an
antireflection film with a thickness of 0.6 μm . A resist
25 composition solution for ArF obtained in Reference Example 1
described later was spin coated onto the antireflection film
and prebaked for 90 seconds on a hot plate at 130°C to obtain

a resist film with a thickness of 0.5 μm . The film was exposed to ArF excimer laser through a mask pattern using an ArF excimer laser exposure apparatus (manufactured by Integrated Solutions Inc., lens numerical aperture: 0.60, wavelength: 193 nm) at an optimum dose. After postbaking on a hot plate at 130°C for 90 seconds, the resist film was developed using a 2.38 wt% tetramethylammonium hydroxide aqueous solution at 25°C for one second, washed with water, and dried to form a positive-tone resist pattern.

10 <Standing wave prevention effect>

Antireflection film formation, resist film formation, exposure, and development were carried out in the above-described manner to observe and evaluate an effect of standing wave on a resist film using a scanning type electron microscope.

<Intermixing prevention effect>

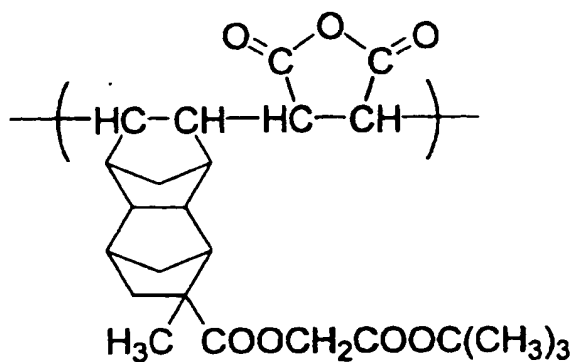
The antireflection film formed according to the above-described procedure was dipped in propyl glycol monomethyl ether acetate for one minute at room temperature. The film thickness was measured before and after dipping using a spectroscopic ellipsometer UV-1280E (manufactured by KLA-Tencor Corp.). The film of which the thickness did not change after dipping was rated as "O" and the film with a thickness change was rated as "X".

25

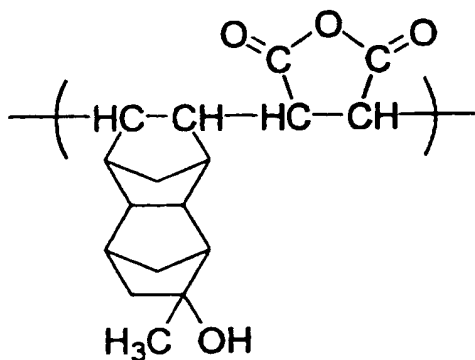
Preparation Example 1

(Preparation of resist composition solution for ArF)

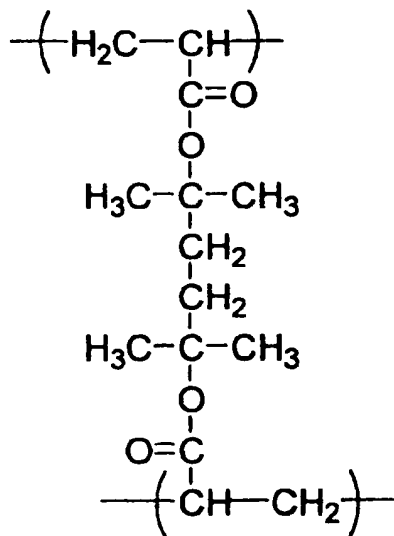
A separable flask equipped with a reflux condenser was charged with 8-methyl-8-t-butoxycarbonylmethoxycarbonyl-tetracyclo[4.4.0.1^{2,5}.1^{7,10}]dodec-3-ene (29 parts), 8-methyl-8-hydroxytetracyclo[4.4.0.1^{2,5}.1^{7,10}]dodec-3-ene (10
5 parts), maleic anhydride (18 parts), 2,5-dimethyl-2,5-hexanedioldiacrylate (4 parts), t-dodecylmercaptan (1 part), azobisisobutyronitrile (4 parts), and 1,2-diethoxyethane (6 parts) in a nitrogen stream. A polymerization reaction was carried out at 70°C for 6 hours.
10 After the polymerization, the reaction mixture was poured into a large amount of a 1:1 (by weight) mixed solvent of n-hexane/i-propyl alcohol to cause the resin to coagulate. The coagulated resin was washed with the solvent several times and dried under vacuum to obtain a resin containing the structural
15 units of the following formula (a), (b), or (c) respectively in the amount of 64 mol%, 18 mol%, and 18 mol%, and having Mw of 27,000 at a yield of 60 wt%.



(a)



(b)



(c)

A resist composition solution for ArF was prepared by dissolving the resulting resin (80 parts), 1-(4-methoxy naphthalen-1-yl)tetrahydrothiophenium nonafluoro-n-butanesulfonate (1.5 parts), tri-n-octylamine (0.04 part) in propylene glycol monomethyl ether acetate (533 parts).

10 Example 2

Synthesis of polymers (III)

A separable flask equipped with a thermometer was charged

with acenaphthylene (8 parts), 5-hydroxymethylacenaphthylene (4 parts), n-butyl acetate (50 parts), and azobisisobutyronitrile (4 parts) in a nitrogen atmosphere. The mixture polymerized at 80°C for seven hours while stirring.

5 The reaction mixture was diluted with n-butyl acetate (100 parts) and the organic layer was washed with a large amount of a mixed solvent of water and methanol (weight ratio 1:2). The solvent was evaporated to obtain a Polymer (III) with an Mw of 1,000.

10

Example 3

Synthesis of polymer (IV)

A separable flask equipped with a thermometer was charged with acenaphthylene (6 parts), 4-hydroxymethyl styrene (5
15 parts), n-butyl acetate (44 parts), and azobisisobutyronitrile (48 parts) in a nitrogen atmosphere. The mixture polymerized at 75°C for seven hours while stirring. The reaction mixture was diluted with n-butyl acetate (100 parts) and the organic layer was washed with a large amount of a mixed solvent of water
20 and methanol (weight ratio 1:2). The solvent was evaporated to obtain a Polymer (IV) with an Mw of 1,200.

Example 4

Synthesis of polymer (V)

25 A separable flask equipped with a thermometer was charged with acenaphthylene (6 parts),
2-hydroxymethyl-6-vinylnaphthalene (5 parts), 2-heptanone (48

parts), and azobisisobutyronitrile (4 parts) in a nitrogen atmosphere. The mixture was polymerized at 75°C for seven hours while stirring. The reaction mixture was diluted with 2-heptanone (100 parts) and the organic layer was washed with
5 a large amount of a mixed solvent of water and methanol (weight ratio 1:2). The solvent was evaporated to obtain Polymer (V) with an Mw of 1,200.

Example 5

10 (Evaluation of antireflection film-forming composition)

The Polymer (III) obtained in Example 2 (10 parts), bis(4-t-butylphenyl)iodonium 10-camphorsulfonate (0.5 part), and 4,4'-[1-{4-(1-[4-hydroxyphenyl]-1-methylethyl)phenyl}-ethylidene]bisphenol (0.5 part) were dissolved in ethyl lactate
15 (89 parts). The solution was filtered using a membrane filter with a pore diameter of 0.1 μm to prepare an antireflection film-forming composition. Properties of the composition were evaluated. The evaluation results are shown in Table 1.

20 Example 6

(Evaluation of antireflection film-forming composition)

The Polymer (III) obtained in Example 2 (10 parts), bis(4-t-butylphenyl)iodonium nonafluoro-n-butanesulfonate (0.5 part), and 4,4'-[1-{4-(1-[4-hydroxyphenyl]-1-
25 methylethyl)phenyl}ethylidene]bisphenol (0.5 part) were dissolved in ethyl lactate (89 parts). The solution was filtered using a membrane filter with a pore diameter of 0.1

μm to prepare an antireflection film-forming composition. Properties of the composition were evaluated. The evaluation results are shown in Table 1.

5 Example 7

(Evaluation of antireflection film-forming composition)

An antireflection film-forming composition was obtained in the same manner as in Example 5, except for using 10 parts of Polymer (IV) obtained in Example 3 instead of 10 parts of
10 Polymer (III) obtained in Example 2. Properties of the composition were evaluated. The evaluation results are shown in Table 1.

Example 8

15 (Evaluation of antireflection film-forming composition)

An antireflection film-forming composition was obtained in the same manner as in Example 6, except for using 10 parts of Polymer (IV) obtained in Example 3 instead of 10 parts of Polymer (III) obtained in Example 2. Properties of the
20 composition were evaluated. The evaluation results are shown in Table 1.

Example 9

(Evaluation of antireflection film-forming composition)

25 An antireflection film-forming composition was obtained in the same manner as in Example 6, except for using 10 parts of Polymer (V) obtained in Example 4 instead of 10 parts of

Polymer (III) obtained in Example 2. Properties of the composition were evaluated. The evaluation results are shown in Table 1.

5 Comparative Example 1

A positive tone resist pattern for KrF and a positive tone resist pattern for ArF were formed without using an antireflection film-forming composition to evaluate the performance. The evaluation results are shown in Table 1.

10

Table 1

	Optical characteristics				Standing wave prevention effect	Intermixing prevention effect
	Wavelength (nm)					
	248		193			
	n-Value	k-Value	n-Value	k-Value		
Example 5	2.2	0.4	1.4	0.4	Yes	O
Example 6	2.2	0.4	1.4	0.4	Yes	O
Example 7	2.0	0.3	1.5	0.6	Yes	O
Example 8	2.0	0.3	1.5	0.6	Yes	O
Example 9	2.2	0.4	1.4	0.4	Yes	O
Comparative Example 1	-	-	-	-	None	X

Acetoxymethylacenaphthylene (1) and
 15 hydroxymethylacenaphthylene (2) of the present invention are particularly suitable for use as raw materials or intermediates for manufacturing Polymer (I).

The Polymer (I) of the present invention is particularly suitable for use as a polymer component for the antireflection
 20 film-forming composition of the present invention.

The antireflection film formed from the antireflection film-forming composition of the present invention exhibits a high antireflection effect and does not cause intermixing with a resist film. Therefore, the antireflection film can form an
5 excellent resist pattern with superior sensitivity, pattern profile, and the like in cooperation with various positive-tone or negative-tone resist compositions. Therefore, the antireflection film-forming composition of the present invention can greatly contribute particularly to the
10 manufacture of high integrated circuits.